The Determination of Trace Metals in Palm Oil Using the GTA-96 Graphite Tube Atomizer

Application Note

Atomic Absorption

Authors

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Introduction

Palm oil is obtained by squeezing fresh nuts from oil palm trees to yield an orange coloured oil with a low free fatty acid content. The oil is bleached either by air (with the oil at 90-95 °C) or by chemical methods. The oil is deodorized of odoriferous impurities by vacuum distillation using superheated steam. Stearin is removed by chilling and filtering off the crystals thus formed [1]. All these processes introduce the possibility of metal contamination which requires monitoring. Graphite furnace atomization compared to flame atomic absorption provides the same advantages for the determination of trace metal content as applies to engine oils [2], namely:

- Small quantities are required

- Complete destruction of the matrix

- Greater sensitivity

- Automatic standard preparation

This article covers the parameters and conditions required for the determination of iron, copper, nickel and lead in palm oil samples and related products after dissolving in DIBK (diisobutylketone, 2,6-dimethylheptan- 4-one). As with engine oil [2], it was discovered that lead could not be determined by atomization from the partition graphite tube (wall atomization). It was found necessary to use a pyrolytic graphite platform.

The analysed samples consisted of crude palm oil, refined bleached deodorized palm oil, degummed palm oil, hydrogenated refined bleached palm oil, hydrogenated fat and stearin.

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Instrumentation

Spectrophometer	Agilent SpectrAA-40
Graphite furnace	Agilent GTA-96 and programmable sample dispenser (sampler)
Lamps	Agilent hollow cathode lamps
Printer	Epson MX-80

The rinse solution for the sampler was an aqueous solution of Triton X-100 (0.01% v/v) and nitric acid (0.1% v/v, 0.015 M). This has already been shown to be an effective rinse solution [3,4] and is more convenient than DIBK.

Standard Preparation

Organometallic standards [5] supplied in a base oil were diluted in DIBK to a suitable concentration for each element. A useful stock concentration was found to be 0.5-1.0 mg/L. The stock was subsequently diluted to give the working solution. The standards are most conveniently made up on a mass per volume basis. The following concentrations of working solutions were used for this study:

Cu	35 µg/L
Ni	64 µg/L
Pb	40 µg/L
Fe	0.69 mg/L (The less sensitive 372.0 nm line of iron was used as the levels present were quite high.)

The total dispensed volume should be less than 15 µL. Larger volumes require very long drying and ashing times to remove all the solvent. The total volume dispensed should be kept constant. This study showed that it is possible to get reliable results with volumes as low as 1 µL provided the dispenser syringe is free of any gas bubbles. A quantity of blank must be added to the sampler program to ensure no solution clings to the dispensing capillary.

Sample Preparation

For the analysis of palm oils, the following suggestions and practical hints should be considered:

In cool climates, the palm oils are all waxy solids which are inconvenient to handle. Placing the sample bottles under an infra-red lamp melts the oils. It is then possible to use a plastic syringe to transfer a sample to a volumetric flask in a drop-wise manner to obtain a required mass. The heavily hydrogenated samples do not melt and must be weighed out as solids.

A trade-off must be made in determining the mass of sample to volume of solution. Too concentrated a solution allows the palm oils to precipitate on standing, the hydrogenated samples being the worst case. Too dilute a solution requires inconveniently large dispensed volumes. A suitable dilution for this study was 1 g sample per 5 mL solution. A warm ultrasonic bath assists dissolving, and storing the solutions at 35 °C helps prevent precipitation. When ambient temperatures are less than 25 °C, an infra-red lamp suspended over the carousel of the Programmable Sample Dispenser helps retard precipitation during analyses.

Other solvents were tried. MIBK (methylisobutylketone, 4–methyl-pentan-2-one) and xylene appear to be as effective as DIBK. ShellSol T, isobutylacetate and heptane were found to be unsuitable.

Results and Discussion

Iron, Copper and Nickel

For all this work, it was found necessary to monitor the background signal by using a deuterium lamp background corrector. Obtaining the best analyte (atomic) signal at atomization requires minimizing the background (non-atomic) signal due to the matrix. This can be achieved by incorporating an ash step to remove the organic matrix. This step is essential for analysing palm oils as even 1 mg generates an impressive plume of soot. If the matrix is not removed before atomization, a large amount of background signal remains. The analyte signal may be masked in extreme cases where the absorbance is much greater than 2.5 Abs.

On the other hand too high an ash temperature, while minimising the background signal, may cause loss of the analyte.

Consequently a study should be carried out for each element to determine the maximum permissible ash temperature before the loss of analyte. In practice it was assumed that all the samples would have similar optimal ash temperatures and individual signal traces tended to confirm this assumption. The general procedure is to increase the ash temperature of the furnace program (steps 5, 6 and 7 in Table 1) and measure the resulting analyte signal and background signal at each ashing temperature. The SpectrAA-40 through its Instrument Operating System [6] allows the process to be speeded up by allowing both the analyte and background signals to be determined on each firing. Typical profiles of absorbance signal against temperature for iron, copper and nickel are shown in Figures 1, 2 and 3 respectively. These show that there is a wide

temperature range between the points where the background signal becomes negligible and where significant analyte signal loss occurs. Any point in this range would be a useful ashing temperature, but, to prolong furnace

Table 1.   General Furnace Program for Iron, Copper, Nickel and Lead in Palm Oil (Optimal Ash Temperature: ***)
(Zero Time in Step 8 Gives Maximum Temperature Ramp Rate.)
(Normal Gas is Argon)

```
OPERATOR        Jonathan  Moffett
DATE            05 September 1985
BATCH           Ni in PORIM Palm Oils.

PROGRAM  19     N i  P a l m  O i l / D I B K

        INSTRUMENT  MODE          ABSORBANCE
        CALIBRATION  MODE         STANDARD  ADD  IT IONS
        MEASUREMENT  MODE         PEAK  HEIGHT
        LAMP  POSITION            4
        LAMP  CURRENT (mA)        8
        SLIT  WIDTH (nm)          0.2
        SLIT  HEIGHT              NORMAL
        WAVELENGTH nm)            232.0
        SAMPLE  INTRODUCTION      SAMPLER  AUTOMIXING
        TIME  CONSTANT            0.05
        MEASUREMENT  TIME (sec)   1.0
        REPLICATES                3
        BACKGROUND  CORRECTION    ON

                  FURNACE  PARAMETERS
STEP    TEMPERATURE    TIME      GAS FLOW    GAS TYPE    READ
NO.        (C)         (sec)     (L/min)                COMMAND
-----------------------------------------------------------------
1          80          5.0        3.0        NORMAL      NO
2          150         30.0       3.0        NORMAL      NO
3          180         20.0       3.0        NORMAL      NO
4          180         10.0       3.0        NORMAL      NO
5          ***         10.0       3.0        NORMAL      NO
6          ***         10.0       3.0        NORMAL      NO
7          ***         2.0        0.0        NORMAL      NO
8          2400        0.0        0.0        NORMAL      YES
9          2400        2.0        0.0        NORMAL      YES
10         2400        2.0        3.0        NORMAL      NO
-----------------------------------------------------------------
```
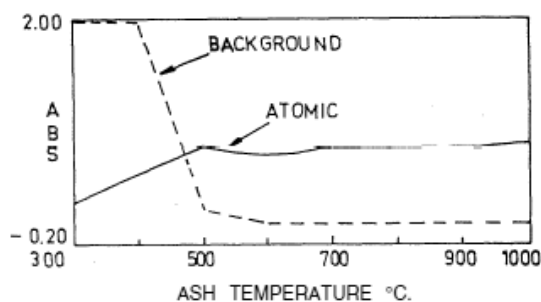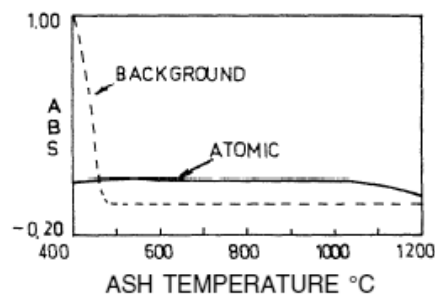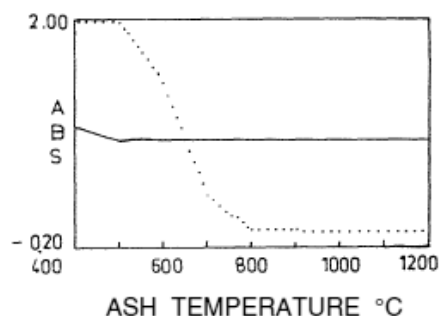

Figure 3.   Ash temperature study of nickel in palm oil.

life, as low a temperature as practicable should be chosen.

The best ash temperatures as determined in this study for iron, copper and nickel in palm oil are listed in Table 2. Representative graphics traces showing well-shaped signal peaks are reproduced in Figures 4(a) and 5(a) respectively. Traces at sub-optimal ash temperature showing very high background signals are reproduced in Figures 4(b) and 5(b) respectively.

Table 2.   Optimal Ash Temperatures for Iron, Copper and Nickel in Palm Oil.

Element	Optimal ash temperatures (°C)
Fe	700
Cu	700
Ni	800

Figure 1.   Ash temperature study of iron in palm oil.

Figure 2.   Ash temperature study of copper in palm oil.
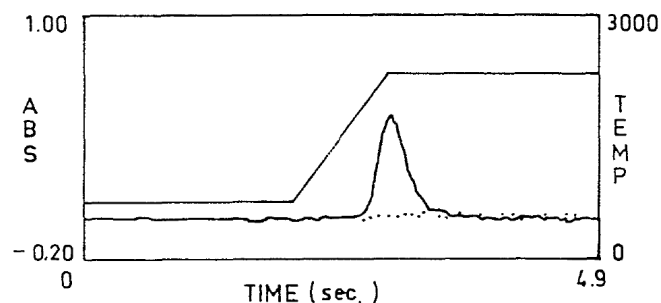

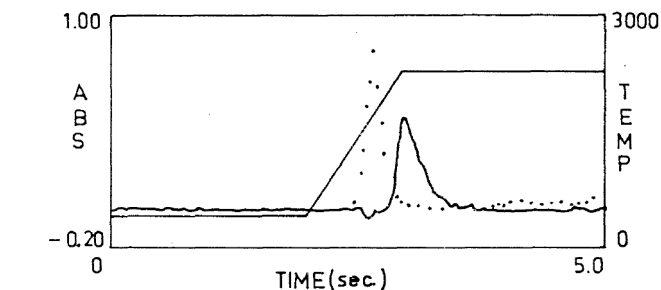Figure 4(a). Signal trace of iron in palm oil at optimal ash temperature.

Figure 4(b). Signal trace of iron in palm oil at sub-optimal ash temperature.
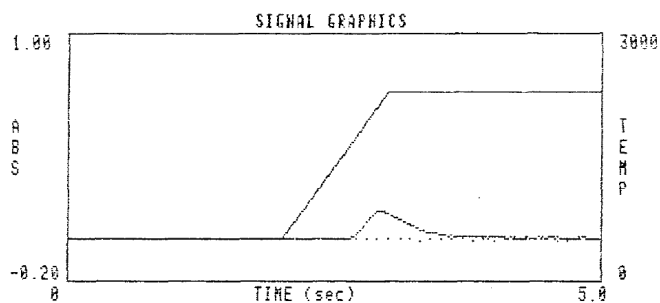(signal:_____ background: ....)

3

Figure 5(a). Signal trace of copper in palm oil at optimal ash temperature.
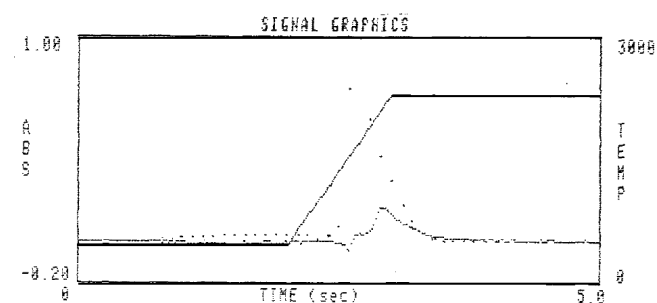

Figure 5(b). Signal trace of copper in palm oil at sub-optimal ash temperature.
(signal:_____ background: ....)

Pb   550

The total mass of palm oil dispensed must not be too large.
5 μL of the recommended dilution represents about 1 mg palm
oil and this should be taken as the upper limit.

The use of argon for ashing is recommended as it gave better
shaped signal eaks and reduced background signals. It is also
a better protecting gas giving longer tube life.

Calibration

For each element, two calibration studies were carried out:
one using the appropriate metal standard in DIBK and the
other using a standards addition program. Results for iron
(Figure 6) show that there is a slight difference between the
two slopes. However copper (Figure 7) and nickel showed sig-
nificant differences in slopes. The graphs for iron and copper
further show in each case that both crude and refined palm
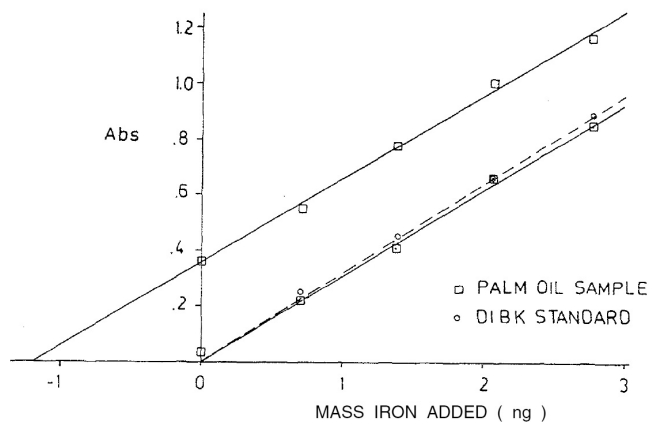oils gave parallel curves.

Figure 6.   Comparison of DIBK standards with standard additions calibration
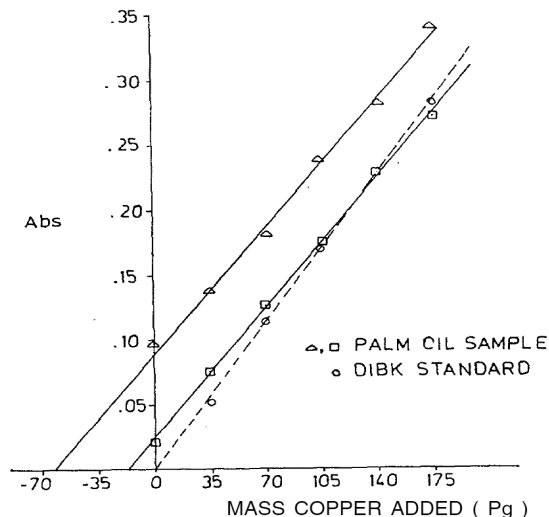curves for iron (peak height).

Figure 7.   Comparison of DIBK standards with standard additions calibration

These results indicate that a standard additions calibration
must be used. The matrix had a constant effect on the slope
which allowed any one sample to be used to calibrate the
rest.

A further study using copper in palm oil was undertaken to
determine if there were any advantages in measuring peak
area rather than peak height. The calibration graph repro-
duced in Figure 8 shows a divergence between the DIBK
standard and the standard additions calibration curves.
Different palm oil samples (which were the same ones used
for the peak height study) gave virtually identical standard
additions calibration slopes in each case. The slopes of the
curves obtained in the two studies are evident in Figures 7
and 8 respectively. From the difference in slopes, it is con-
cluded that the peak height measurement is about three
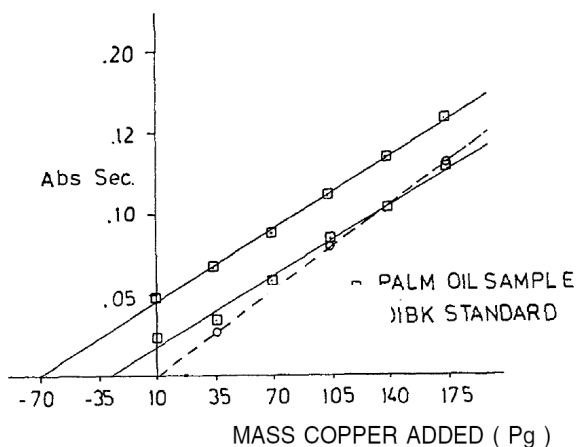times more sensitive than peak area.

4

Figure 8. Comparison of DIBK standards with standard additions calibration curves for copper (peak area).

To summarize, for these elements the peak height measuring mode should be used. Initial calibration must be done using a standard additions method on one sample. This can be used as a calibration curve for the rest of the samples. The standard additions program feature of the Programmable Sample Dispenser considerably simplifies this procedure as only one standard needs to be made up. Typical programs are shown in Tables 3(a), 3(b) and 4.

Table 3(a). Sampler Parameters for Iron and Copper in Palm Oil

| | SAMPLER PARAMETERS VOLUMES (uL) | | | |
	STANDARD	SAMPLE	BLANK	MODIFIER
BLANK	- -	- -	12	
ADDITION 1	1	5	6	
ADDITION 2	2	5	5	
ADDITION 3	3	5	4	
ADDITION 4	4	5	3	
ADDITION 5	5	5	2	
SAMPLE	- -	5	7	

RECALIBRATION RATE	0

MULTIPLE INJECT	NO	HOT INJECT	NO	PRE INJECT	NO

Table 3(b). Sampler Parameters for Nickel in Palm Oil

| | SAMPLER VOLUMES (uL) | | | |
	STANDARD	SAMPLE	BLANK	MODIFIER
BLANK	--	--	12	
ADDITION 1	2	5	5	
ADDITION 2	4	5	3	
SAMPLE	--	5	7	

RECALIBRATION RATE	8

MULTIPLE INJECT	NO	HOT INJECT	NO	PRE INJECT MOD	NO

Table 4. Sampler Parameters for Lead in Palm Oil

| | SAMPLER PARAMETERS VOLUMES (uL) | | | |
	STANDARD	SAMPLE	BLANK	MODIFIER
BLANK	--	--	13	
ADDITION 1	2	5	6	
ADDITION 2	4	5	4	
ADDITION 3	6	5	2	
SAMPLE	--	5	8	

RECALIBRATION RATE	0

MULTIPLE INJECT	NO	HOT INJECT	NO	PRE INJECT	NO

Standard addition calibration curves obtained experimentally are reproduced for iron (Figure 9), copper (Figure 10) and nickel (Figure 11). Precision for iron and copper was typically better than 5% relative standard deviation (RSD). Precision for nickel was typically better than 10% RSD in the absorbance range 0.01 to 0.15.
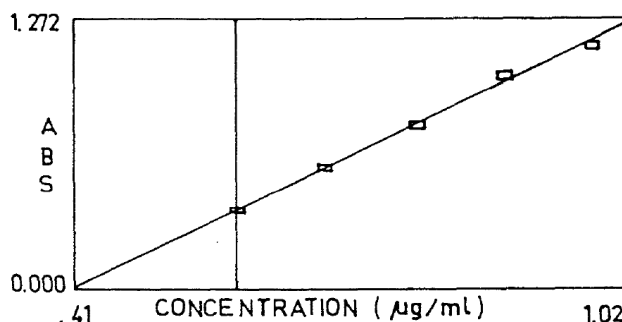

Figure 9. Standard additions calibration curve for iron in palm oil (single replicate).
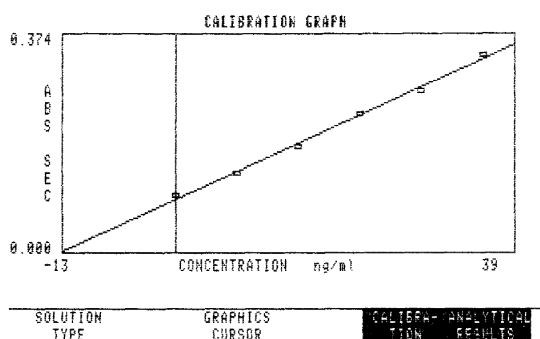

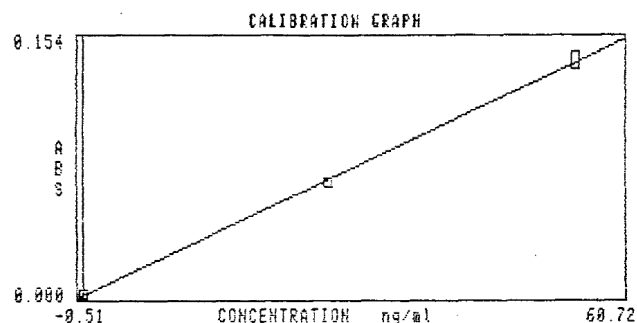Figure 10. Standard additions calibration curve for copper in palm oil (single replicate).

Figure 11. Standard additions calibration curve for nickel in palm oil (triple replicates).

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Lead

Attempts to use the partition graphite tube in this study gave unsatisfactory results. It was not possible to ash the sample successfully without losing lead, as shown in previous work [2,4]. Lowering the ash temperature resulted only in very high background signals (> 2.5 Abs) and poor signal peak shape. The DIBK solution precludes the use of modifiers such as ammonium dihydrogen orthophosphate.

Using a pyrolytic graphite platform [7] inside a plateau graphite tube allowed the same form of ash study as for the other metals. A similar furnace program can also be employed (Table 1). The major difference is the need for a higher atomization temperature to ensure the platform is thoroughly cleaned to achieve well-shaped analyte signal peaks. An air ash step was added after atomization, as a precaution in ash temperature studies, to remove any remaining soot (Table 5).

Results of an ash temperature profile study are shown in Figure 12. Unlike the other metals, there is a narrow margin in temperature between minimum background and significant analyte loss. It was determined that the best ash temperature is 550 °C. Experiments with different temperature ramp rates showed that the maximum rate (2000 °C/s) gave the best results.
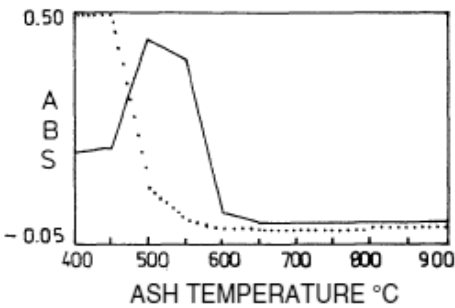

Figure 12.   Ash temperature study of lead in palm oil.

A calibration study showed that as for copper and nickel the matrix does have an effect on the calibration for lead in palm oil. This has been observed previously [8]. A representative signal trace obtained at optimal ash temperature is reproduced in Figure 13. A calibration curve obtained by using the program in Table 4 is reproduced in Figure 14. The precision of measurement for lead was similar to that for nickel.

Table 5.   Furnace Program for Ashing Studies on Lead in Palm Oil (Normal gas is Argon; Alternate gas is air).

```
DATE           23 September 1985
BATCH          Pb in Palm Oil (Pre-cal)

PROGRAM 8      Pb Palm Oil


       INSTRUMENT  MODE          ABSORBANCE
       CALIBRATION  MODE         STANDARD ADDITIONS
       MEASUREMENT MODE          PEAK HEIGHT
       LAMP  POSITION            6
       LAMP CURRENT (mA)         5
       SLIT WIDTH (nm)           0.5
       SLIT HEIGHT               NORMAL
       WAVELENGTH (nm)           283.3
       SAMPLE  INTRODUCTION      SAMPLER  AUTOMIXING
       TIME CONSTANT             0.05
       MEASUREMENT  TIME (sec)   1.0
       REPLICATES                3
       BACKGROUND  CORRECTION    ON
```

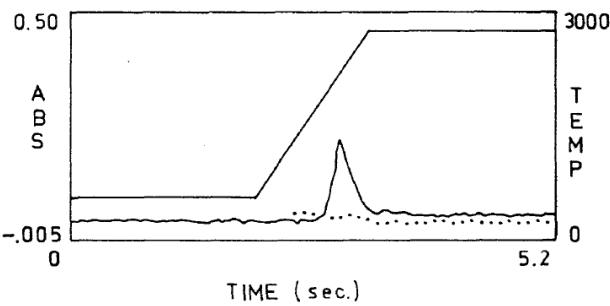| STEP NO.	TEMPERATURE (C)	FURNACE PARAMETERS TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	30	5.0	3.0	NORMAL	NO
2	150	20.0	3.0	NORMAL	NO
3	180	10.0	3.0	NORMAL	NO
4	180	10.0	3.0	NORMAL	NO
5	550	10.0	3.0	NORMAL	NO
6	550	30.0	3.0	NORMAL	NO
7	550	2.0	0.0	NORMAL	NO
8	2800	1.2	0.0	NORMAL	YES
9	2800	2.0	0.0	NORMAL	YES
10	2800	2.0	3.0	NORMAL	NO
11	400	12.0	3.0	NORMAL	NO
12	400	10.0	3.0	ALTERNATE	NO
13	80	1.6	3.0	NORMAL	NO

Figure 13.   Signal trace of lead in palm oil at optimal ash temperature. (signal:_____ background:..........)
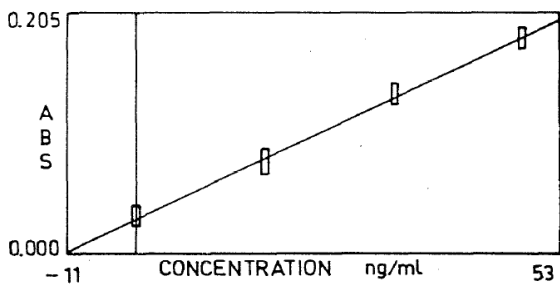

Figure 14.   Standard additions calibration curve for lead in palm oil (triple replicates).

Summary

Palm oil can be conveniently analyzed for trace metals using a graphite tube atomizer. Lead (and probably other volatile elements) can be determined using a pyrolytic graphite platform in a plateau graphite tube. For less volatile elements such as iron, copper and nickel, the sample solution can be dispensed directly onto the wall of a partition graphite tube. All the elements studied showed varying matrix effects and a calibration curve must be established by the standards additions technique, preferably using the programmable features of the sampler. Precision for each element depends on the sensitivity and concentration in the palm oils. For iron and copper, precision was typically better than 5% RSD and for nickel and lead, typically better than 10%.

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